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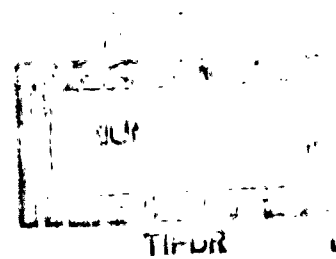Office of Naval Research, Washington, D.C.

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STRESS CORROSION CRACKING

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This report summarizes the principal results of research done under contract with O.N.R., with references to reports issued during the period covered by the contract.

Crack propagation in various alloys

The overall impression gained from a study of the literature was that there is considerable disagreement and uncertainty about the qualitative way in which stress corrosion cracks propagate in metals, especially stainless steels. This matter is of prime importance, since it would indicate which property of the alloy should be investigated in order to determine the mechanism of stress corrosion fracture. Thus if a crack propagates in a manner which involves primarily brittle fracture, then the factors which embrittle the alloy concerned should be analyzed. On the other hand, if a crack is formed by the continuous dissolving away of the metal along a very narrow path as the crack opens, then the electrochemical behavior and structure of the metal undergoing the rapid attack would require investigation.

Experimental work was undertaken, therefore, to study the qualitative nature of crack propagation in various alloys. The methods used to detect instantaneous mechanical contributions to cracking included detailed measurement of electrochemical potential changes and of extension

in length of wire specimens during cracking, as well as recording the sound, if any, generated during cracking. The data which were obtained[1]* led to the conclusion that crack propagation in austenitic stainless steel and in a magnesium-base alloy is a gradual process without any indication of steps of sudden fracture. Mild steel in nitrate solutions was found to crack in an uneven manner, and exhibited alternating periods of slow and rapid propagation. The rapid stages, however, did not attain the speed of a brittle fracture. Aluminum-magnesium and aluminum-copper alloys exhibited crack propagation in alternating steps of electrochemical corrosion and instantaneous physical fracture. The slow advance of cracks in stainless steel, mild steel and the magnesium-base alloy is consistent with an electrochemical mechanism. Extremely small mechanical steps in the crack propagation process, however, may have escaped detection with the experimental techniques available. Thus the existence of periodic brittle fracture steps on a microscopic scale is not precluded by the results of this investigation.

Crack initiation and immunity

Pure nickel, high-Ni alloys and some purified low-Ni austenitic stainless steels are apparently immune to stress corrosion cracking in hot chloride solutions. The apparent immunity could result from the inability of these solutions to initiate cracks on the surface of the metal. If cracking were to be initiated artificially, propagation of the crack might be induced in an apparently immune alloy.

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*See list of references below.

To investigate this possibility, duplex materials were made having a thin layer of a crack-susceptible alloy bonded to a thick layer of the apparently-immune alloy. Commercial 304 or 347 stainless steel was used for the susceptible layer. On pure nickel[2] or on an immune purified 16 Cr - 20 Ni stainless steel[4], all stress-corrosion cracks induced in the susceptible alloy stopped on reaching the bonding interface. As a check, similar bonding of the susceptible layer was made to other 16 Cr - 20 Ni alloys made mildly susceptible by Mo or N additions. In these cases some of the cracks generated in the commercial alloy layer continued on through the interface and slowly penetrated the 16 - 20 alloy. It may be concluded that metals which are immune to stress corrosion cracking will not support the crack propagation process, and that no cracking would be induced in the stressed metal even if a corrodent were used which produced very sharp stress-raising pits.

Electrochemical factors

A relatively long period of electrochemical corrosion is generally required to "develop" or uncover crack-initiation sites. For stainless steels in hot chloride solutions this period varies from 1 to 100 hours or more. Once a crack is initiated the propagation process, although gradual, usually requires a much shorter time.

A comprehensive electrochemical study was made[3] to determine whether the anodic processes during the initiation phase exhibit any distinct differences from a susceptible to a non-susceptible alloy. In

addition, forced corrosion at constant potential (potentiostatic corrosion) was compared in an attempt to accentuate any differences. An improved cell was designed for electrochemical measurements under conditions of greater precision and control. The behavior of a commercial 18-8 alloy, highly susceptible to cracking, was compared in detail with that of an unsusceptible pure 16 Cr - 20 Ni alloy, using boiling 42% $MgCl_2$ as corrodent.

It was found that the application of stress had no appreciable affect on the corrosion of the unsusceptible alloy. Stress also had little effect on the susceptible alloy during the initiation period, and within this period the latter corroded in approximately the same potential range and with the same average anodic current densities as did the unsusceptible alloy. Increasing stress, however, did shorten the initiation period, as well as the crack-propagation period, for the susceptible alloy.

By means of potential-current curves it was established that crack propagation is accompanied by enhanced anodic dissolution. The corrosion reaction itself may not be a sufficient condition for sustained propagation, however. One cannot exclude the possibility that a periodic brittle - fracture step, on a microscopic scale, accompanies the anodic metal-dissolution process.

Potentiostatic corrosion measurements clearly demonstrated that the anodic process necessary for crack propagation can be slowed down or stopped by fixing the potential at appropriate values.[3] Even after the normal stress corrosion process was allowed to proceed until cracks

of appreciable length developed, a relatively small shift of the potential
in the less noble direction was sufficient to prevent further propagation.
Thereafter the partly cracked specimen remained cathodically protected and
did not fail under continuous tensile stress.[1]

For stainless steels stressed above the yield point in boiling
42% $MgCl_2$, the potential normally moved during the initiation period
50 to 80 mv in the more noble direction from its initial value. When the
potential was fixed at the initial value, stress corrosion cracking was
prevented. If the potential was raised 50-80 mv at the beginning of corrosion,
the initiation stage was essentially eliminated and cracking was rapid,
the number of cracks produced being two orders of magnitude greater than
the number obtained without potential control. Thus it was demonstrated
that potentiostatic corrosion, at a fixed potential less than 100 mv more
noble than the initial value, could be used as a cogent accelerated test
for susceptibility to stress corrosion cracking.[3]

Anodic polarization at a yielding surface

Crack propagation is a gradual process. Hence it could result
from an entirely electrochemical mechanism without any brittle-fracture
component. For an entirely electrochemical mechanism, however, the
propagation rates observed require that the anodic current density at
the root of the crack be rather high (the order of 1 amp/cm^2). One
recent theory assumes that yielding metal, such as that at the root of a
crack, must exhibit unusually low anodic polarization in a susceptible

alloy. Metals which are not susceptible to stress corrosion cracking would not exhibit this depolarization due to yielding.

As yet there is little direct evidence in support of this theory. Experimental work was carried out to measure directly the anodic depolarization resulting from yielding.[4] A cell was designed which permitted very large strain rates of wire specimens in a rapidly moving corrodent. Potential measurements were made while the entire surface of the wire was yielding. It was found that a relatively small anodic depolarization effect was produced by the yielding process. There was little difference in the magnitude of the effect, however, with either highly susceptible commercial stainless steels or with unsusceptible metals such as pure nickel or purified 16 Cr - 20 Ni stainless steel. It may be concluded that the act of yielding is not in itself sufficient to produce crack propagation by enhanced anodic dissolution.

Effects of stainless steel composition

Two series of stainless steel alloys were investigated, most of them prepared at Westinghouse Research Laboratories for this study. One series was based on 20% Ni - 16% Cr - bal. Fe, the other on 14% Ni - 16% Cr - bal. Fe. Alloys were made by systematic additions of single impurity elements in concentrations up to 6%. A few alloys having multiple additions were also prepared.

I. - Based on 20 Ni - 16 Cr: a) 8 vacuum-melted alloys

b) 10 air-melted alloys

c) 17 levitation-melted alloys

II. - Based on 14 Ni - 16 Cr: a) vacuum-melted (parent) alloy

b) 40 levitation-melted alloys.

It was found that low concentrations of several impurity elements had a profound influence on stress corrosion cracking in boiling 42% $MgCl_2$. In the 20% Ni series, the purest vacuum-melted alloy (0.01C, 0.01N) was immune to cracking during the maximum test period (250 hours). Additions of manganese or carbon or both preserved this immunity. Silicon (0.5%) added with manganese also left the alloy apparently immune. Nitrogen (as little as 0.03%) and molybdenum imparted susceptibility, the time to complete fracture decreasing with increasing concentration. The effects of these elements could be counteracted by raising the carbon content; roughly 0.4% C was generally sufficient to regenerate complete resistance to cracking.

Such distinct effects of impurities were not as readily observable in the 14% Ni series, because the purified parent alloy itself cracked readily. The beneficial effect of carbon addition was clearly demonstrated, however. Approximately 0.1% C appeared to be sufficient to remove all susceptibility to cracking. The addition of 0.1% Pt was detrimental and accelerated the stress corrosion cracking process.

Data were obtained on high-nickel alloys, and were in accord with published reports that the high nickel content (above 40%) imparts immunity to stress corrosion cracking. It may be concluded from the

present work, however, that susceptibility to stress corrosion cracking in alloys of lower nickel content is not fixed by the Ni - Cr - Fe ratio, but depends upon added "impurity" elements.

Concluding remarks

The effects of minor alloying elements on stress corrosion cracking poses some fundamental problems, including:

1. The distribution of impurity elements, their effects on the microstructure of the alloy, and their role in creating crack-initiation sites.

2. Possible migration of impurity elements towards the metal-solution interface in the plastically deformed zone at the root of a growing crack.

3. The influence of impurities on anodic polarization at the root of a crack. (According to a recently advanced theory, local areas of solute segregation give rise to enhanced chemical and electrochemical activity.)

Some preliminary work along these lines was initiated using a group of high-purity 16 Cr - 20 Ni stainless steels each containing one added impurity. Solute-segregated areas have not yet been demonstrated. Electron microscope pictures of the root of the crack were taken at 15,000 magnification. These revealed that cracks, which at lower magnification appeared to grow perpendicular to the axis of tensile stress, showed marked deviations from this direction near the root. Some cracks had branched roots, and in many cases sharp changes in direction of the crack occurred at twin boundaries.

It may be anticipated that future research aimed at correlating the structural role of minor elements with their influence on localized electrochemical activity will contribute directly to a complete mechanism of stress corrosion cracking.

References

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